Direct atmospheric evidence for the irreversible formation of aqueous secondary organic aerosol (aqSOA)

Marwa M.H. El-Sayed, Yingqing Wang and Christopher J. Hennigan (hennigan@umbc.edu)

Department of Chemical, Biochemical and Environmental Engineering, University of Maryland, Baltimore County

Overview and Objective

Recent evidence indicates that the uptake of water-soluble organic gases ($WSOC_g$) into atmospheric waters – likely represents an important pathway for secondary organic aerosol (SOA) formation [1]. This aqueous SOA (aqSOA) can help in explaining the current underprediction of SOA concentrations by many state-of-the-art models [2].

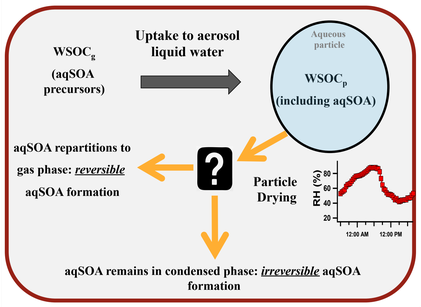

Figure 1 Schematic of aqSOA formation in aerosol water.

A central component of this study was an analysis of the behavior of particulate water-soluble organic carbon ($WSOC_p$) under conditions of aerosol drying (liquid water evaporation).

Fundamental aspects of aqSOA formation remain uncertain or unknown including uncertainties in the relative contributions of reversible and irreversible uptake processes.

The purpose of this study was to investigate the reversible/irreversible nature of aqSOA using direct atmospheric observations.

Ambient Measurement Overview:

- **Baltimore, MD**
- **3-30 September, 2014**

Experimental Setup

1. CO analyzer
2. OCEC analyzer
3. Data acquisition
4. PILS
5. TOC analyzer
6. Mist Chamber
7. 3-way valve
8. Ambient channel
9. Dry channel

Figure 2 Experimental set-up placed in an enclosure on the rooftop.

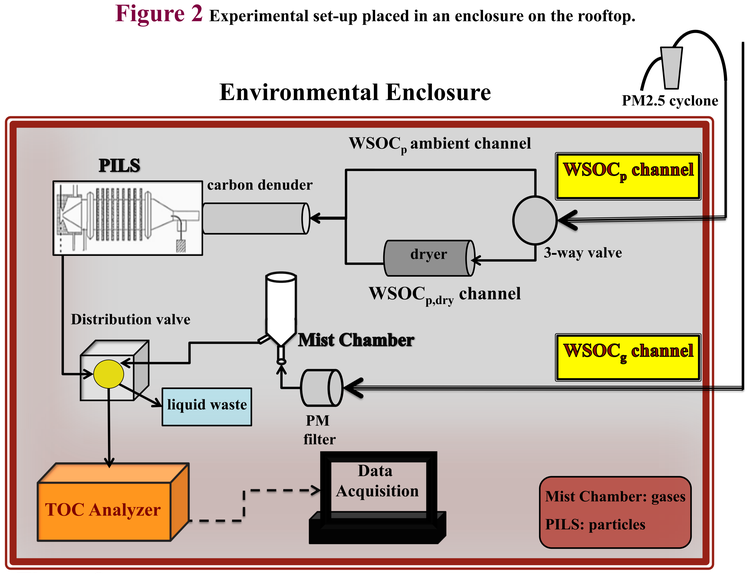

Figure 3 Schematic of experimental set-up. A $WSOC_g$ – $WSOC_p$ – $WSOC_{p,dry}$ cycle was completed every 14 min.

Effect of Temperature on $WSOC_g$ and $WSOC_p$

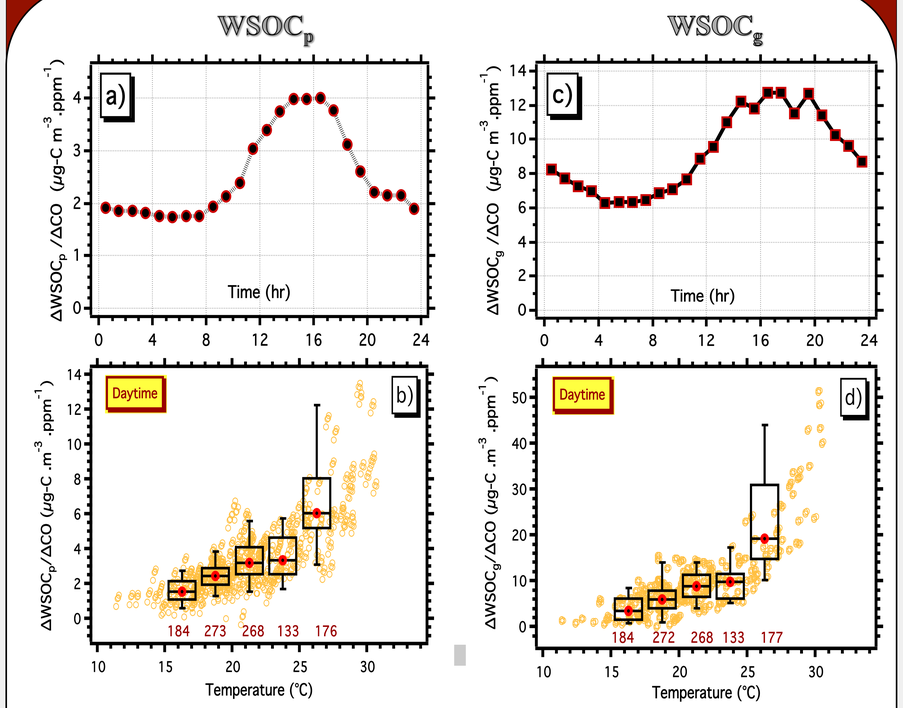

Figure 4 Average diurnal profiles of $\Delta WSOC_p/\Delta CO$ (a) and $\Delta WSOC_g/\Delta CO$ (c). Boxplots of daytime $\Delta WSOC_p/\Delta CO$ (b) and daytime $\Delta WSOC_g/\Delta CO$ (d) as a function of temperature.

WSOC in both the gas- ($WSOC_g$) and particle ($WSOC_p$) phases increased exponentially during the day with the increase in temperature, highlighting the effect of photochemistry on SOA production.

Evidence for Nighttime aqSOA Formation

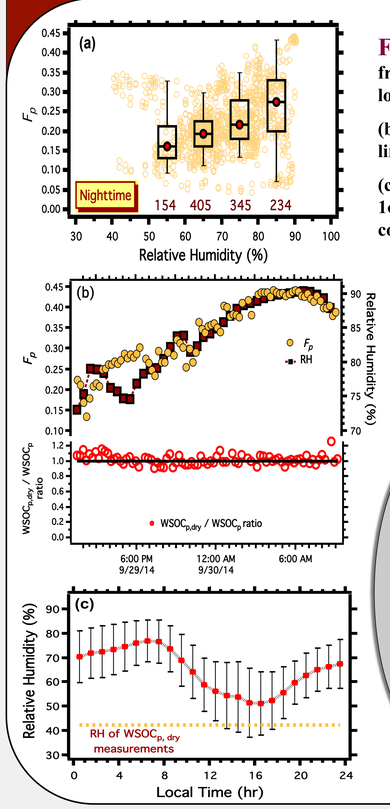

Figure 5 **(a) Scatter and box plots of the particulate WSOC fraction, F_p, as a function of RH at nighttime (20:00 to 07:00, local time).**

(b) Event beginning on 29 September 2014. The black solid line at $WSOC_{p,dry}/WSOC_p$ ratio = 1 is for visual reference.

(c) Average diurnal profile of RH (vertical bars represent +/- 1σ). The dotted line at 42.5% RH represents the average RH conditions for the $WSOC_{p,dry}$ measurement.

$$F_p = \frac{WSOC_p}{WSOC_g + WSOC_p} \quad (3)$$

- The fraction of WSOC in the particle phase, F_p, increased with increasing relative humidity (RH) during the nighttime_a statistically significant increase according to the Student's t-test.
- aqSOA formation occurred during the night through the absorption of $WSOC_g$ in liquid water.

Assessing Reversibility of aqSOA Partitioning

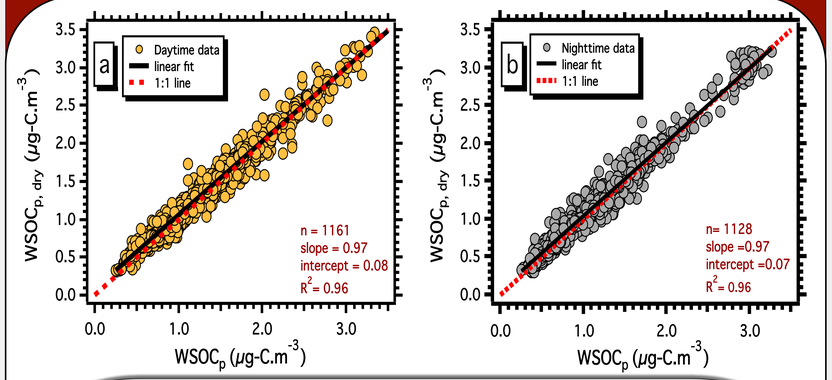

Figure 6 Scatter plots of $WSOC_{p,dry}$ versus $WSOC_p$ for daytime (a) and nighttime (b); and linear regression results using least squares regression analysis.

There was no statistically significant difference in the $WSOC_p$ measurements through the dry and ambient channels for either daytime or nighttime periods.

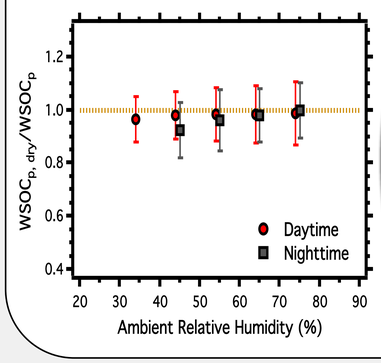

Figure 7 Median daytime and nighttime values of the $WSOC_{p,dry}/WSOC_p$ ratio as a function of ambient RH.

The $WSOC_{p,dry}/WSOC_p$ ratio was unity - within experimental error - across all ambient conditions encountered during the study.

No statistical difference between $WSOC_p$ and $WSOC_{p,dry}$ was observed as a function of RH.

Conclusions and Future Work

- SOA formation was observed primarily due to two pathways: 1) daytime photochemical SOA production, and 2) nighttime aqSOA production.
- SOA formed through the uptake of $WSOC_g$ into aerosol liquid water under dark conditions remained in the particle phase upon the evaporation of aerosol water, i.e. the observed aqSOA was formed irreversibly [4].
- Methods used in this study will be deployed across multiple seasons to characterize a wider range in meteorology, source influences and aerosol composition.
- A range of drying times will be investigated outside of the 7-s used in this experimental setup.

Acknowledgments

This work was supported by the National Science Foundation through award 1464458.

References

1. Ervens, B., B. J. Turpin, and R. J. Weber (2011), Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, 11(21), 11069-11102.
2. Volkamer, R., *et al.* (2007), A missing sink for gas-phase glyoxal in Mexico City: Formation of secondary organic aerosol, *Geophys. Res. Lett.*, 34(19).
3. Hennigan, C. J., *et al.* (2008), Enhanced secondary organic aerosol formation due to water uptake by fine particles, *Geophys. Res. Lett.*, 35(18).
4. El-Sayed, M.H., *et al.* (2015), Direct atmospheric evidence for the irreversible formation of aqueous secondary organic aerosol (aqSOA), *Geophys. Res. Lett., In press*.